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## PATENT SPECIFICATION

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### (54) IMPROVED SLOW SET PECTIN AND PROCESS FOR PREPARING SAME

(71) We, GENERAL FOODS CORPORATION, a Corporation organized under the laws of the State of Delaware, United States of America, of 250, North Street, White Plains, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to manufacture of pectin.

Among other trade designations, pectins are frequently characterized as being rapid-setting or slow-setting. Typically, the rapid-setting pectins, standardized to 150 grade, have a degree of methylation (D.M.) in the range of 68 to 83. Slow-setting pectins, also standardized to 150 grade, usually have a D.H. of 60 to 65 and the setting temperature of these pectins in a jelly at 65% by weight soluble solids and pH of 3 may vary between 125° and 155°F. Generally, slow-setting pectins are prepared by pectin manufacturers by demethylating pectin employing isopropyl alcohol with either sulfuric acid or hydrochloric acid as the catalyst. During this demethylation step, the pectin is converted from one having a D.M. of approximately 68 to 76 to a pectin with a D.M. of approximately 61 to 63. A typical, commercially available slow-set pectin may have the following approximate distribution of total carboxyl groups, based on the total number of galacturonic acid units: methyl esters — 60 to 65%; free carboxyls — 17.5 to 20%; and sodium or ammonium salts — 17.5 to 20%. When employed in the manufacture of jellies, jams and preserves, many of the available slow-set pectins are characterized by their sensitivity to alkaline earth metal and also by their rather high setting temperatures. For example, slow-set pectins with sensitivity toward alkaline earth metal may react with divalent and trivalent metal ions, particularly calcium ions, which are present in fruit juices. A decreased sensitivity towards alkaline earth

ions is therefore a sensitivity which is less than that of these known slow set pectins. Under certain conditions of pectin concentration, temperature, PH and sugar concentration a premature gelation of the pectin may take place. The results of the interaction between such pectin and alkaline earth metal especially in the vacuum pan processing of jellies, jams and preserves, is a lessening of the gel strength or even a complete failure of the final product which is, of course, undesirable. The reasons why such slow-setting pectin exhibits this sensitivity to alkaline earth metal or possesses 'calcium sensitivity' as the phenomenon is frequently characterized, is not completely understood. However, it is theorized that the spatial arrangement of the free carboxyl groups within the pectin molecule may play a role but is also believed that the presence of even a small fraction of a low D.M. pectin, that is, a pectin having a D.M. of about 3 to 7, may have an effect. In addition to the calcium sensitivity of slow-set pectin, many of such pectins are characterized by setting temperatures which are rather high. Inasmuch as low setting temperatures would offer economy and ease of processing in jelly, jam and preserve manufacture, there is a definite need for a slow-set pectin with much lower setting temperatures, for example, in the range of about 120°F. or less.

It has now been discovered that slow-set pectin may be prepared by contacting pectin with an ammoniacal alcohol solution at low temperatures. By this process one is obviously able to obtain a pectin having a D.M. of 60 to 70 with markedly improved tolerance towards alkaline earth metal ions such as calcium and a pectin which will set at temperatures of about 120°F. or less. Thus, the process is particularly well adapted to provide a less calcium sensitive pectin whose ability to form a gel at low temperatures is enhanced. While the theory underlying the mechanism involved in obtaining the improved slow-set pectin of this invention is not completely understood, it seems that demethylation in

ammoniacal alcohol brings about the random introduction of acid amide groups and possibly also ammonium salt moieties into the pectin molecule thereby possibly blocking the carboxyl groups in the molecule with the result that premature gel formation due to the influence of alkaline earth metal is avoided.

According to the invention therefore, there is provided a process for preparing a slow-set pectin having a  $-\text{CONH}_2$  group content of 3 to 6 per cent, based on the total number of galacturonic acid units, which comprises contacting pectin having a D.M. (as herein defined) of at least 71 at a temperature of less than  $50^\circ\text{F}$ . with an ammoniacal alcohol solution at a concentration sufficient and for a period of time sufficient to demethylate said pectin to a D.M. of 60 to 70.

The demethylation in ammoniacal alcohol is carried out at a temperature of less than  $50^\circ\text{F}$ . and it has been discovered that this range of temperatures for demethylation is particularly critical in attaining of a pectin having decreased calcium sensitivity as herein defined and lower setting temperatures as herein defined. A range of demethylation temperatures between  $-5^\circ\text{F}$ . and  $50^\circ\text{F}$ . is also found to be particularly desirable inasmuch as operating at these low temperatures preserves pectin grade and improves grade-pH performance.

Typically, the improved slow-set pectin of this invention may have the following approximate distribution of total carboxyl groups, based on the total number of galacturonic acid units:  $\text{COOCH}_3$  — 60 to 70%,  $\text{COOH}$  — 26 to 37%, and  $\text{CONH}_2$  — 3 to 6%. With reference to this distribution of the total carboxyl groups and with that of heretofore available slow-set pectins, the pectin of this invention may be seen to have a certain number of carboxyl groups converted to amide groups and possibly also ammonium salt groupings. It appears that the ratio of methoxyl ( $\text{COOCH}_3$ ) groups to amide ( $\text{CONH}_2$ ) groups in the slow-set pectin of this invention is determinative in pectin product performance in a jelly in terms of grade-pH and setting temperature characteristics.

The pectin starting material to be employed in the process of this invention may be obtained from a variety of sources as, for example, citrus fruit peels and apple pomace. Moreover, the pectin so employed may have a rather high D.M. due to the source material or to the method of extraction utilized. In this connection high D.M. pectins appear quite suitable provided they are not inherently calcium sensitive.

In the preparation of slow-set pectin of this invention, it may also be advantageous to first treat pectin with acidified methyl alcohol solution to increase D.M. and also to insure a non-calcium sensitive pectin and

to minimize grade loss during later demethylation. The pectin to be so treated may be in the form of dried particles or wet or dried shreds which are prepared as extruded noodles or as a hydrated gel. Alternatively, the pectin to be employed may be one obtained as a precipitate as, for example, by having been treated with an alcohol or certain metal salts. While any of such types of pectin are suitable, the process of this invention is particularly well adapted to be employed using a pectin-metal co-precipitate as the starting material. Thus, such co-precipitate is conventionally obtained in pectin manufacture after the raw material, usually citrus fruit peel, is hydrolyzed and extracted. The extract is filtered and clarified and is then precipitated with a solution of a metal salt such as copper sulfate, aluminum sulfate, copper chloride, aluminum chloride and the like or mixtures. The co-precipitate, commonly called "green" and having a moisture content of about 88%, is treated with an acidified methyl alcohol solution. While other acids may be used, such as hydrochloric acid or phosphoric acid, sulfuric acid is especially preferred and it is by this step of the process the degree of methylation of the pectin is increased to approximately 71 to 76 D.M. Following the treatment with acidified alcohol solution, the pectin which is now essentially free of metals which have been co-precipitated with pectin may be washed with alcohol and water. The pectin may then be separated from the treating and washing solutions and is contacted with an ammoniacal alcohol solution at a temperature of less than  $50^\circ\text{F}$ . The ammoniacal alcohol solution will typically comprise 1% ammonia, 39% water and 60% methyl alcohol but ammonia concentrations of 0.5 to 3%, and methyl alcohol concentrations of 60 to 80% may be used. After contacting the pectin with the ammoniacal alcohol solution for a period of for example 6 to 24 hours, preferably 8 to 12 hours, at between  $-5^\circ$  and  $50^\circ\text{F}$ ., preferably about  $0^\circ\text{F}$ ., the pectin is demethylated to 60 to 70 D.M. The pectin so obtained is then washed with alcohol for example as a water-alcohol solution and is further treated with an acid alcohol solution to adjust pectin pH thereby converting some of the salt ( $\text{COONH}_2$ ) groups on the pectin molecule to the acid ( $\text{COOH}$ ) form. The so-adjusted pectin is then subjected to a drying operation as, for example, vacuum drying, for a period of 6 to 9 hours.

It is apparent that in treating the pectin with an acidified alcohol solution, methyl alcohol must be employed inasmuch as it is desired to increase the degree of methylation of the pectin while at the same time to remove co-precipitating metals, if present, therefrom. On the other hand, during the demethylation step a large number of alcohols besides methyl alcohol such as ethyl alcohol, isopropyl alcohol

and the like and mixtures thereof may be employed. However, methyl alcohol is preferred since it offers the advantage of ease in operations and also in any solvent recovery procedures.

In order to illustrate the present invention, the following nonlimiting examples are given:

#### EXAMPLE I.

Into a suitable blender are placed 1000 parts of a pectin-copper sulfate-aluminum sulfate co-precipitate. The coprecipitate is washed with 5000 parts of a solution comprising 5% sulfuric acid, 67% methyl alcohol and the balance water. After washing for one-half hour, the co-precipitate is then treated with a second solution comprising 8.3% sulfuric acid, 79% methyl alcohol and the balance water for 6 to 10 hours at 85°F. The pectin now having a D.M. of approximately 71 to 76, is then leached for two hours with a third solution comprising 2% sulfuric acid, 60% methyl alcohol and the balance water. The pectin is then leached with a neutral 60% alcohol-water solution for two hours to remove trace amounts of acid and color. The leached pectin is next contacted with a solution comprising a 1% ammonia, 60% methyl alcohol and the balance water at 50°F. for 10 hours. Subsequently, the pectin now having a D.M. of 60 to 63 is rinsed twice with a 60% methyl alcohol-water solution and is then pH adjusted with a slightly acidified 60% methyl alcohol solution for about one-half hour. Following

an additional rinsing with a 90% methyl alcohol-water solution, the pectin is dried for four hours at 125°F. The analysis on the pectin so obtained is as follows:

Weight %	OCH <sub>3</sub> , as is	7.9	
Weight %	COOH, as is	6.2	40
Weight %	NH <sub>3</sub> , as is	0.4	

Total carboxyl distribution, based on the total number of galacturonic acid units, is:

COOCH <sub>3</sub>	61%	
COOH	33%	45
CONH <sub>2</sub>	6%	
Equivalent Weight	557	
I.F.T. Grade*, as is	207	
I.F.T. Grade, dry basis	223	
Setting Time **	10 minutes	50

\* Method described in Food Technology, 1959, Vol. XIII, No. 9, pages 496-500.

\*\* Method described in Food Technology, Vol. III, January 1949, pages 18-22, by Joseph and Baier.

The pectin was then evaluated in a series of samples of 65% soluble solids sugar jellies employing commercially available slow-set pectins (identified as A, B and BB) as controls. A comparison of the pectins for calcium sensitivity, setting temperature, setting time and overall characteristics of the jellies so prepared is tabulated below:

	Calcium* Sensitivity	Setting Temperature	Setting Time	Slice Strength*** (Grape Jelly)
Product of Example I	Low	110°F	10 min.	101 cms.
Product A	High	140°F.	4.5 min.	60 cms.
Product B	Medium	130°F.	4.5 min.	86 cms.
Product BB	Medium	130°F.	4.5 min.	88 cms.

\*\*\*Method described in Analytical Chemistry, Vol. 21, March 1949, pages 409-411, by W. A. Bender.

\*Calcium sensitivity is measured by the ability of the gel to stand after overnight cure. A sensitive pectin may be almost liquid.

#### EXAMPLE II.

The procedure of Example I is repeated in all essential respects except that the demethylation step is carried out at 32°F. for six hours employing a 2% ammonia-methyl alcohol-water solution. The total carboxyl distribution, based on the total number of galacturonic acid units, of the pectin so obtained is shown to be COOCH<sub>3</sub>, — 66.1;

COOH — 29.4%; and CONH<sub>2</sub>, — 4.5%. The pectin is characterized by its low calcium sensitivity and by a setting temperature of 95°F.

#### EXAMPLE III.

The procedure of Example I is repeated in all essential respects except that the demethylation step is carried out at 0°F. for

Sample No.	Reaction Conditions <sup>1</sup>			Carboxyl Distribution as			IFT Grade (Dry Basis)	1% Viscosity (Centipoises)	Setting		Carb Sensitivity (Minimum, hours)
	T <sup>1</sup> F	%NH <sub>4</sub>	Hours	COOH	COOH	CONH <sub>2</sub>			Time, Seconds	T <sup>1</sup> F	
X-4597 <sup>f</sup>	59	1.0	5.10	67.5	28.4	4.1	244	35.1	375	121	5
X-4698 <sup>f</sup>	50	0.9	6.80	67.6	28.1	4.3	244	44.1	330	124	5
X-4699	32	0.9	15.00	67.7	27.9	4.4	254	63.4	335	128	5
X-4691	3	3.0	10.00	67.1	25.8	7.1	253	84.2	440	100	5

<sup>1</sup>Comparative runs.

Sample No.	3.05 Jelly <sup>2</sup> pH			3.10 Jelly <sup>2</sup> pH		
	Slice Strength (Centimeters)	% Pectin Savings		Slice Strength (Centimeters)	% Pectin Savings	
X-4697	72	6.7		78	9.5	
X-4698	89	17.4		93	18.9	
X-4699	98	23.2		95	20.2	
X-4693	116	34.7		106	26.9	

NOTE: 1. A 60 percent methyl alcohol concentration was employed in the reaction mixture and a portion of the same methylated pectin shreds was used in each of the demethylation reactions.

2. The jellies were made with 30 percent less 150-grade pectin or the assumption the pectin grade was greater than 150, for example, 150 ÷ .70 = 214.4.

These results effectively demonstrate significant end product variation with reaction temperature. Thus, pectins demethylated at decreasingly lower temperatures do impart a much improved gel texture to a finished gel as indicated by slice strength values. Also, it is noted that there is a trend to higher grade, lower setting temperature and higher viscosity with lower reaction temperatures. These properties are affected by depolymerization —

the lower the temperature, the less the depolymerization.

It is further observed that as the reaction temperature is lowered, more amide groups can be put on the pectin molecule for a given D.M. Setting temperature, setting time and breaking strength are significantly affected — setting temperature is lowered; setting time is slower; and less pectin is required for any given slice strength.

The potential economic implications are apparent from the data with respect to "% Pectin Savings". Since commercial jellies generally run around 70 to 80 centimeter slice strength, the data shows, for example, at a jelly pH of 3.10 that about 27% less of pectin demethylated at 3°F. is necessary to match the gel texture of jellies prepared from two commercially available slow-set pectin products. Also, the data shows that pectin reduction is approximately doubled by lowering the reaction temperature from 59° to 50°F.

While this invention has been described by reference to specific examples, it is to be understood that it is not to be limited thereto. Thus, for example, the process for preparing the improved slow-set pectin may be carried out in a continuous, as well as a batchwise, manner.

#### WHAT WE CLAIM IS:—

1. A process for preparing a slow-set pectin having a  $-\text{CONH}_2$  group content of 3 to 6 per cent, based on the total number of galacturonic acid units, which comprises contacting pectin having a D.M. (as herein defined) of at least 71 at a temperature of less than 50°F. with an ammoniacal alcohol solution at a concentration sufficient and for a period of time sufficient to demethylate said pectin to a D.M. of 60 to 70.

2. A process according to claim 1, in which the ammonia concentration of said ammoniacal alcohol solution is from 0.5 to 3.0% volume

by volume and said period of time is from 6 to 24 hours.

3. A process according to either of claims 1 and 2, further comprising first treating said pectin with an acidified methyl alcohol solution to methylate said pectin to at least a D.M. of 71 and then separating said pectin therefrom prior to contacting said pectin with said ammoniacal alcohol solution.

4. A process according to claim 3, further comprising washing said separated pectin with an alcohol prior to contacting said pectin with said ammoniacal alcohol solution.

5. A process according to either of claims 3 and 4, in which the alcohol used for washing and the ammoniacal solution is methyl alcohol.

6. A process according to any one of claims 1 to 5, in which said pectin is in the form of a pectin-metal coprecipitate.

7. A process according to any one of claims 1 to 6, further comprising separating said pectin having a D.M. of 60 to 70, treating said pectin with an acid and vacuum drying.

8. A process according to claim 7, further comprising washing said separated pectin having a D.M. of 60 to 70 with an alcohol prior to treating said pectin with said acid.

9. A process of preparing an improved slow set pectin substantially as hereinbefore described in the Examples.

10. A slow set pectin when produced by a process as claimed in any one of claims 1 to 9.

11. A slow-set pectin with low setting temperature as herein defined and with decreased sensitivity toward alkaline earth metal ions as herein defined having a D.M. of 60 to 70, and a  $-\text{CONH}_2$  group content of 3 to 6 per cent, based on the total number of galacturonic acid units.

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